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THE DIELECTRIC CONSTANTS OF TERNARY MIXTURES

By

ERNEST George EHLMAN

A Thesis Submitted for the Degree of

MASTER OF ARTS

UNIVERSITY OF WISCONSIN

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Considerable work has already been done on dielectric constants in this University by Schlundt[1], Eggers[2], Mathews[3], and Anthony[4], but nothing has been done on ternary mixtures, so far as the writer can learn, either here or elsewhere.

Eggers has already given a brief account of methods employed in determining dielectric constants, and Mathews has furnished a complete bibliography, so that a repetition of either would be superfluous.

At the suggestion of Dr. Kahlenberg, a study of dielectric constants of ternary mixtures was made. Water, the universal solvent of high dielectric constant, was chosen as one of the liquids, and pyridine, of low dielectric constant, was chosen as the second liquid because it is miscible with water in all proportions and is a solvent for many organic substances. It was thought best to mix water and pyridine in three proportions by weight; namely, 25% water, 50% water, and 75% water, so that a third liquid might dissolve in at least one of the three mixtures, the object being to involve as much water as possible, thus showing more definitely the influence on the high dielectric constant of water. In spite of the choice

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1. Bull, Univ. of Wis. Science Series, 2353(1901).
2. Jam. Phys. Chem., Vol.8, No.I.Jan.: p.14 (1904).
3. " " " " 9 , No.8,Nov.: p.641(1905).
4. Jour. de Chim. Phys., Vol. 4, No.8, Oct,: p.358 (1906).

thus afforded, many organic substances, among them cymene, xylene, and carbontetrachloride, were practically insoluble in any of the three mixtures, due entirely to the presence of water.

The apparatus used was similar to that described by Drude[1] under method (2), in which only small quantities of liquids are necessary. The principle is based upon the resonance of electrical waves along wires in secondary circuits, an elementary treatise of which is presented clearly in Watson's Physics[2] The complete mathematical treatment of this principle is given by Drude[3]. For the calibration of the apparatus, seventeen liquids recommended by Drude[4]were prepared--mixtures of acetone and water for high dielectric constants, and mixtures of benzene and acetone for low dielectric constants, and from these results a curve was plotted, using dielectric constants as ordinates and distances in centimeters as abscissas.

As a check on these results, Drude's[5]second series of liquids was prepared, and the known dielectric constant of each liquid compared with that obtained from the curve. Also,a number

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1. Zeit. Phys. Chem., Vol. 23, p. 267 (1897).

2. Watson's Physics, p. 880.

3. Drude: Phys. des Aethers auf Elektromag. Grundlage, Ch.IX.

4. Zeit. Phys. Chem. Vol. 23, p. 267 (1897)

5. Landolt: Bornstein Meyerhoffer Phys.-Chem. Tabel. pp. 239.

of compounds of known dielectric constants were first rectified and their values found to coincide closely with those obtained from the curve. It was necessary to use sixteen volts with variable resistance in series in order to run the apparatus.

After the instrument was adjusted, it was noticed that many factors modified the adjustment, either causing a displacement of the original zero, or weakening the luminosity of the resonance tube. It would perhaps be well to mention them.

First, the width of the spark gaps, of which two are in kerosene, and one in air, must be kept constant; second, the adjustable portion of apparatus in kerosene oil must not be lowered or raised; third, the level of the kerosene should be kept constant; fourth, the accumulation of carbon caused by the discharge in the kerosene should be removed, either by filtering or by complete replacement; fifth, the spring of the interrupter should be kept under the same pressure as nearly as possible; and sixth, the E. M. F. and current should be constant.

Several condenser bulbs were made with platinum wires sealed in their sides leaving an air gap of from 2 to 4 millimeters. These bulbs were carefully tested, and those were selected for use which gave the greatest range. It was noticed that when the platinum wires were thin, they were easily bent, thus changing the width of the air gap inside and in this way changing the capacity. Thick wires are there-

fore necessary.

Even with minimum E. M. F., the illumination of the resonance tube extended through too great a range for the securing of accurate results, therefore, some device was necessary to overcome this defect. This was accomplished by placing an additional wire near and parallel to the one marked B in Drude's[1] apparatus. A new set of waves resulted which interfered with the original set, cutting down the range as well as the intensity. The former is an advantage, while the latter is a slight disadvantage when dealing with liquids which absorb the waves to any great extent. When this wire was placed close to B, the intensity was at a maximum, when moved away from B, the intensity diminished until complete interference took place, and no resonance was possible.

In determining the dielectric constant, ten readings were taken for each liquid. If the results varied more than five millimeters, a second and third set were taken. The condenser bulb each time was cleansed with alcohol, then with ether, and finally dried before introducing another liquid. Each time it was necessary to redetermine the zeros of the apparatus in order to be sure that no change had taken place in the adjustment. This was effectively done by using the empty bulb at 200 cm. for one extreme, water at 50 cm. for

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1. Zeit. Phys. Chem., Vol.23, p.269 (1897).

the other extreme, and acetone for an intermediate point; if these three checked, the instrument was certainly in adjustment.

After one set of readings was taken, the bulb was again filled with the same liquid and the dielectric constant determined. Well water, lake water, and laboratorywater were distilled and compared as to conductivity. The laboratory water, showing the least conductivity, was used for these experiments. All of the liquids were redistilled. Where there was a possibility of the presence of water, they were first dried with fused calcium chloride. Pyridine was dried with caustic soda. All of the liquids except the carbondisulphide were either Schuchardt's or Kahlbaum's preparations.

The specific gravity, the specific conductivity, the boiling point, and the dielectric constant of each liquid were determined. When the boiling point was not constant, as in the case of some of the nitriles, a fraction of the liquid was collected near the proper boiling point. Such liquids are indicated in Table I. by a dash between the figures representing their boiling points.

The liquids were mixed by using burettes and pipettes of small bore graduated in tenths of cubic centimeters, it

being thus an easy matter to estimate to 1/20 of a cu. cm.

Kohlrausch's method was used for determining conductivities. When the conductivities of a group varied peculiarly, they were redetermined by adding the liquid in question to the mixture of pyridine and water already in the Kohlrausch vessel, the increase or decrease in conductivity being noted with the increase of the solute.

When a liquid was found which was not miscible in all proportions with the pyridine solution, enough was added to saturate the solution. This will account for the short curves in the drawings, represented by heavy lines; the dotted lines being interpolations.

Difficulty was experienced at the outset in getting constant conductivities and constant dielectric constants for the pyridine and water mixtures, since on standing the conductivities increased, and the dielectric constants in general decreased.

The variation increased with the per cent of water present. Therefore the conductivities and the dielectric constants of the pyridine and water mixtures were redetermined for each liquid used. This will account for discrepancies in the data used for the conductivities and dielectric constants of the pyridine and water mixtures.

A similar variation was noticed in most of the ternary mixtures, it being most marked when the resulting mixtures gave a greater conductivity than any of the ingredients, and this change in value was greater in the conductivities than in the dielectric constants. For this reason measurements of ternary liquids were taken immediately after mixing the liquids.

Pyridine and water showed considerable contraction on mixing. (See specific gravity in Table I.)

Table I. was included for the use of others who might wish to continue work along this line.

From the data in Table II. curves were plotted using dielectric constants for ordinates, and per cents by weight for abscissas. The following abbreviations are used:

W...........water.
P..........pyridine.
Sp.C.......specific conductivity.
D.C........dielectric constant.
T..........temperature.
B.Pt.......boiling point.
Bar........barometric pressure.
Sp.Gr......specific gravity.
Sp.V.......specific volume.
<..........less than.

TABLE I.

COMPOUND	Symbol	B.Pt.	Bar.	Sp.Gr.	Sp.Vol.	T.
Water	H_2O	99	73.8	.998	1.002	21
Wat. 25% Pyr. 75%				1.020	.9804	20
" 50% " 50%				1.029	.9716	20
" 75% " 25%				1.042	.9597	20
Pyridine	C_5H_5N	114	73.8	.976	1.0246	22
Benzene	C_6H_6	78.8	74.2	.8771	1.1400	20
Carbondisulphide	CS_2	45	73.8	1.2673	.7890	22
Aniline	C_6H_7N	179	73.45	1.0227	.9778	20
Ethyl Acetate	$C_4H_8O_2$	75	74.4	.8942	1.1183	20
Toluene	C_7H_9N	108.5	74.2	.8648	1.1563	24
Methyl Acetate	$C_3H_6O_2$	55	74.2	.9265	1.0765	22
Triethylamine	$(C_2H_5)_3N$	75	74.3	.7587	1.3150	22
Ethyl Lactate	$C_5H_{10}O_3$	151-3	72.9	1.0246	.9760	22
Isobutylnitrile	C_5H_9N	104	73	1.1830	.8450	22
Ethylcyan Acetate	$C_5H_7O_2N$	103-6	73	1.0777	.9280	24
Ethyl Malonate	$C_7H_{12}O_4$	192-5	73.5	1.0493	.9530	24
BenzylCyanide	C_8H_7N	225-6	73.5	.9722	1.0280	24
Benzonitrile	C_7H_5N	186	74.5	1.0049	.9950	24
Piperidine	$C_5H_{11}N$	105	74.5	.8655	1.1554	20

TABLE II.

MATERIAL.	Sp. C.	T.	D.C.	T.
	GROUP 1.			
Water	6.7×10^{-6}	19	80.4	19
75% W.. 25% Pyr.	10×10^{-6}	"	63.1	"
50% " 50% "	7×10^{-6}	"	46.5	"
25% " 75% "	2.8×10^{-6}	"	32.5	"
Pyridine	$<12 \times 10^{-6}$	20	12.4	22
	GROUP 2.			
8% Benzene in 75% W. 25% P.	$.1 \times 10^{-6}$	19	63.1	21
	GROUP 3.			
2% Benzene in 50% W. 50% P.	7×10^{-6}	19	45	21
3% " " " " " "	6.9×10^{-6}	"	44.2	"
	GROUP 4.			
2% Benzene in 25% W. 75% P.	2.8×10^{-6}	19	32	20
5% " " " "	2.7×10^{-6}	"	31.1	"
10% " " " "	2.5×10^{-6}	"	29.3	"
18% " " " "	1.9×10^{-6}	"	25.6	"
Benzene	$<.12 \times 10^{-6}$	"	2.3	"
	GROUP 5.			
25% W. 75% P.	3.4×10^{-6}	19	32.5	21
3% Carbondisulphide " " "	6.9×10^{-6}	"	32.5	"
10% " " " "	11×10^{-6}	"	30.8	"
11% " " " "	12×10^{-6}	"	30.7	"
Carbondisulphide	$<.12 \times 10^{-6}$	"	2.6	"

TABLE II.

MATERIAL	Sp. C.	T.	D.C.	T.
GROUP 6.				
25%W,75%P.	3×10^{-6}	18	32.5	19
21.7% Aniline &" "	2.5×10^{-6}	"	27.5	"
45.4% " " "	1.7×10^{-6}	"	19.7	"
71.4% " " "	$.73 \times 10^{-6}$	"	11.4	"
Aniline	$<.12 \times 10^{-6}$	"	6.9	"
GROUP 7.				
50%W,50%P	14×10^{-6}	19	46.5	19
10% Ethyl Acetate &" "	15×10^{-5}	"	41.5	"
30% " " " "	18×10^{-6}	"	32.	"
50% " " " "	18.5×10^{-6}	"	23.	"
Ethyl Acetate	$<.12 \times 10^{-6}$	"	6.1	"
GROUP 8.				
25%W,75%P.	$38. \times 10^{-6}$	19	32.5	19
5% Toluene & " "	3.8×10^{-6}	"	30.5	"
10% " " "	3.2×10^{-6}	"	28.5	"
12% " " "	3.1×10^{-6}	"	27.6	"
17.2% " " "	2.4×10^{-6}	"	24.1	"
Toluene	$<.12 \times 10^{-6}$	"	2.3	18.5
GROUP 9.				
50%W,50%P.	$9. \times 10^{-6}$	19	48.5	22
5 % Aniline &" "	8.5×10^{-6}	"	45.3	"
15 % " " "	8.3×10^{-6}	"	39.2	"
21.2% " " "	8.3×10^{-6}	"	35.	"
Aniline	$<.12 \times 10^{-6}$	"	6.9	"

TABLE II.

MATERIAL	Sp.C.	T.	D.C.	T.
GROUP 10.				
75%W,25%P.	1×10^{-5}	19	64.5	20
10% Methyl Acetate &" "	31×10^{-5}	20	60.5	"
40% " " " "	22×10^{-5}	"	39.8	"
70% " " " "	11×10^{-5}	"	20.9	"
Methyl Acetate	$.039 \times 10^{-5}$	"	7.	"
GROUP 11.				
75%W,25%P.	1×10^{-5}	19	63.	21
10% Triethylamine &" "	50×10^{-5}	"	51.7	"
40% " " "	7.4×10^{-5}	"	31.8	"
70% " " "	1.3×10^{-5}	"	17.2	"
Triethylamine	$< .12 \times 10^{-6}$	"	4.7	"
GROUP 12.				
75%W,25%P.	1×10^{-5}	20	61.	21
10% Ethyl Lactate &" "	150×10^{-5}	"	49.4	"
30% " " " "	130×10^{-5}	"	42.2	"
60% " " " "	120×10^{-5}	"	31.8	"
Ethyl Lactate	1.3×10^{-5}	"	8.2	"
GROUP 13.				
75%W,25%P.	1×10^{-5}	20	61.	21
5% Isobutylnitrile" "	50×10^{-5}	"	59	"

TABLE II.

MATERIAL	Sp.C.	T.	D.C.	T.
GROUP 13 (Cont.)				
12%Isobutylnitrile &75%W,25%P.	77 x 10^{-5}	20	52	21
20% " " "	100 x 10^{-5}	"	47.2	"
Isobutylnitrile	.1 x 10^{-5}	"	21	"
GROUP 14.				
50%W,50%P.	7 x 10^{-6}	20	47	21
10% Ethylcyan Acetate" "	300 x 10^{-6}	"	47	"
20% " " " "	800 x 10^{-6}	"	45	"
30% " " " "	3000 x 10^{-6}	"	39.8	"
Ethylcyan Acetate	7.6 x 10^{-6}	"	20.6	"
GROUP 15.				
25%W,75%P.	6 x 10^{-6}	20	32.5	21
10% Ethyl Malonate & " "	30 x 10^{-6}	"	30.8	"
40% " " " "	50 x 10^{-6}	"	23.1	"
70% " " " "	60 x 10^{-6}	"	13.1	"
Ethyl Malonate	$<.12$ x 10^{-6}	"	7.7	"
GROUP 16.				
25%W,75%P.	6 x 10^{-6}	20	32.5	21
10% Benzyl Cyanide & " "	60 x 10^{-6}	"	31.5	"

TABLE II.

MATERIAL	Sp.C.	T.	D.C.	T.
GROUP 16.(CONT.)				
30%BenzylCyanide & 25%W,75%P.	70×10^{-6}	20	27.3	21
42% " " " "	280×10^{-6}	"	24.7	"
Benzyl Cyanide	3×10^{-6}	"	1.7	"
GROUP 17.				
25%W,75%P.	7.6×10^{-6}	20	34.5	22
10% Ethyl Acetate & " "	18×10^{-6}	"	32.5	"
40% " " " "	31×10^{-6}	"	21.1	"
70% " " " "	30×10^{-6}	"	13.6	"
Ethyl Acetate	$< 1.2 \times 10^{-7}$	"	6.1	"
GROUP 18.				
25%W,75%P.	7.6×10^{-6}	20	34.4	22
10% Benzonitrile & " "	15×10^{-6}	"	32.7	"
20% " " "	19×10^{-6}	"	32.1	"
42% " " "	29×10^{-6}	"	30.6	"
Benzonitrile	14×10^{-6}	"	24.8	"
GROUP 19.				
Pyridine	$< 1.2 \times 10^{-7}$	20	12.4	22
10% Triethylamine & "	7×10^{-7}	"	11.8	"

TABLE II.

MATERIAL	Sp.C.	T.	D.C.	T.
	GROUP 19(Cont.)			
40% Triethylamine & P.	7×10^{-7}	20	9.4	22
Triethylamine	$<1.2 \times 10^{-7}$	"	4.7	"
	GROUP 20.			
75%W,25%P.	3×10^{-5}	20	65.	22
20% Piperidine & " "	30×10^{-5}	"	54.5	"
50% " " "	32×10^{-5}	"	31.5	"
70% " " "	35×10^{-5}	"	17.	"
Piperidine	$<1.2 \times 10^{-7}$	"	5.	"

Group 1, pyridine and water, gave nearly a straight line, as shown in Curve 1. The conductivity of 25% pyridine is greater than that of pure water; but with an increase of pyridine it becomes less, yet it is far greater than that of pyridine. It will be remembered that pyridine has basic properties, therefore increased conductivity is not surprising.

Groups 2 and 3. Benzene was only slightly soluble and had little effect upon the conductivity or the dielectric constant.

Groups 4, 5, and 8 were plotted together, as shown in Curve 4. The dielectric constant of carbondisulphide, benzene, and toluene are about the same, yet the curves show quite a difference in the effect upon the dielectric constant of the solvent. They happen to be arranged in the order of their specific gravities. The curve of the carbondisulphide falls upon the straight line joining the dielectric constants of solvent and carbondisulphide, consequently the others fall below or have a greater influence on the dielectric constant of the solvent. The conductivities of benzene and toluene run parallel with their dielectric constants. That of carbondisulphide does not.

Groups 6 and 7, aniline and ethyl acetate, are plotted together in Curve 3. The curves cross each other in three dif-

ferent places, showing considerable irregularity. The conductivity for aniline runs in the same direction, but for ethyl acetate it runs in the opposite direction. In such a case as this, where the conductivity is greatly increased, by the addition of more of the solvent a point is reached at which the conductivity is finally decreased.

Groups 7 and 9, ethyl acetate and aniline, are represented in Curve 2, showing a slight divergence. It was mentioned before that dotted lines are interpolated. Comparing this curve with Curve 3, in which the same solutes are used, the solvent differing in per cent of water, it is apparent that such a difference in per cent may cause a considerable change in the shape of the curve, in other words, the influence upon the same solutes might be reversed in direction. In both cases of aniline, the conductivities run parallel with the dielectric constants, while with ethyl acetate this is not true.

Group 10 and 11, methyl acetate and triethylamine, are represented in Curve 5. Here considerable divergence is noticed at first, the curves gradually converging and then running parallel. The conductivities are enormously increased by the addition of the solutes, and in the case of triethylamine, the absorption is very pronounced. Triethylamine in pyridine alone did not show this absorption; the increased conductivity

and absorption indicate the presence of an alcohol due to saponification.

Groups 12 and 13, ethyl lactate and isobutylnitrile, shown in Curve 6, have the same characteristics as the preceding group.

Group 14, ethylcyan acetate, shown in Curve 7, has the same characteristics, but with greatly increased conductivity.

Groups 15, 16, 18, and 20, ethyl malonate, benzyl cyanide, benzonitrile, and piperidine, have similar characteristics, but with very little absorption.

Conclusions.

1. Of the seventeen groups studied, only four have their conductivities running parallel with their dielectric constants.

2. Pronounced absorption was accompanied by increased conductivity, though when increased conductivity was present, absorption did not necessarily occur.

3. Undoubtedly saponification takes place in some instances, thus accounting for increased conductivity and increased absorption.

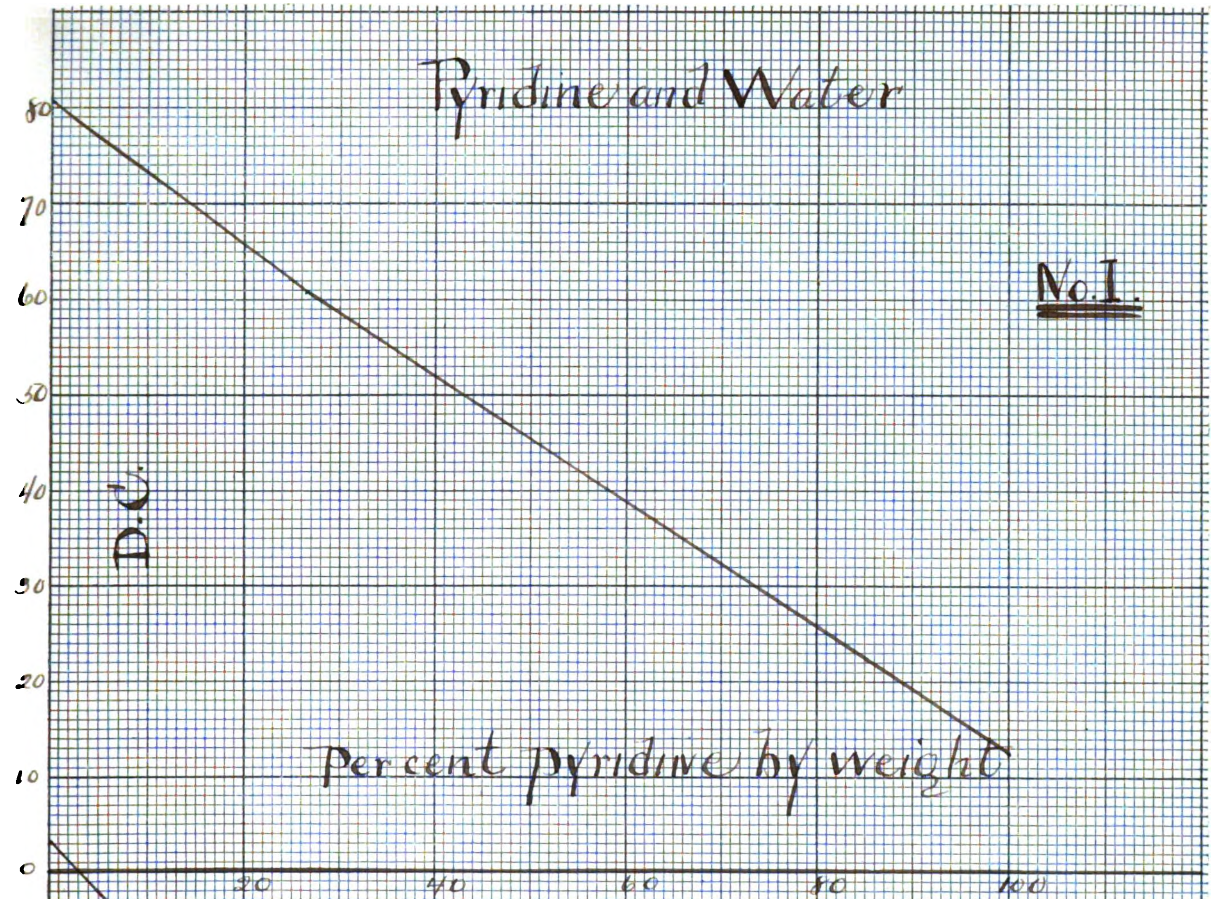
4. A comparison of curves of solutes having the same dielectric constants, well illustrated in Curve 4, shows that the nature of the solute and solvent determine the form of

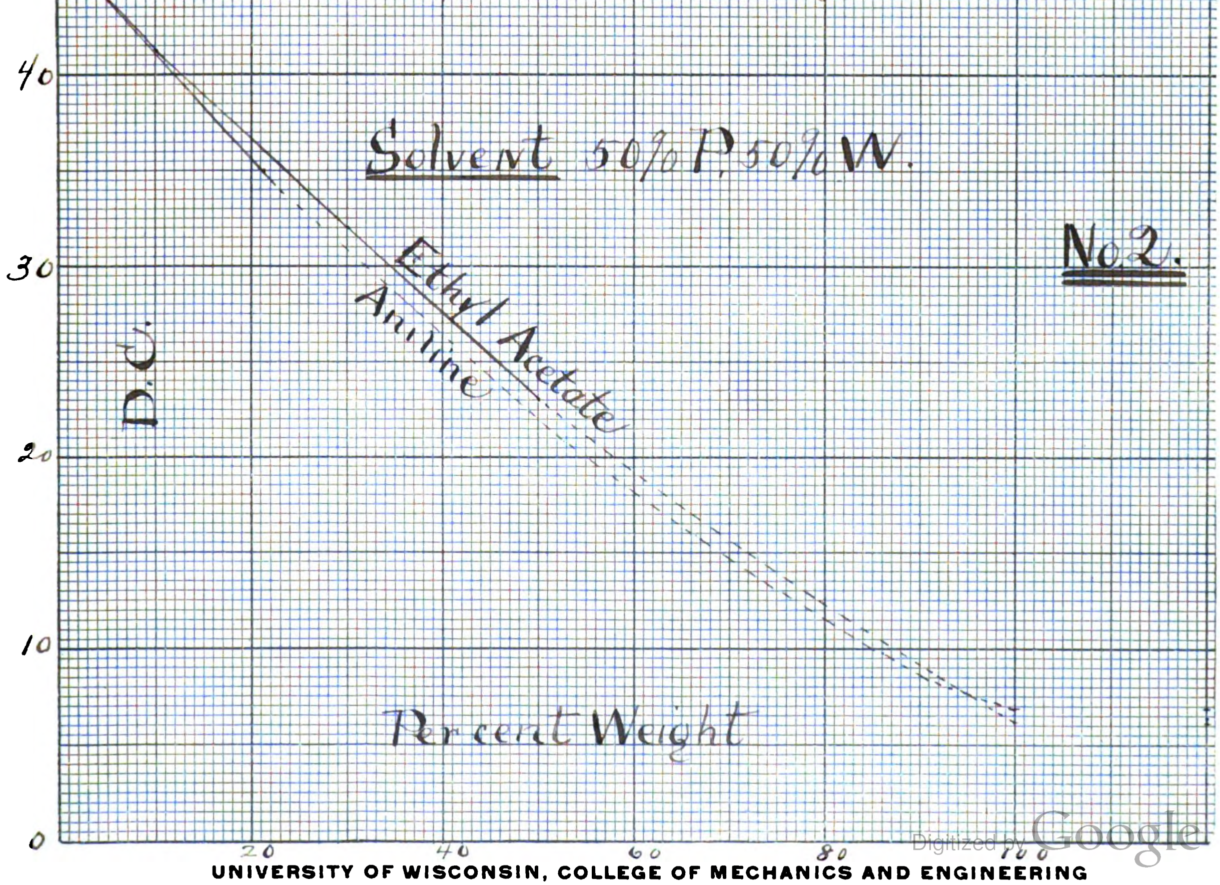
curve, or the dielectric constants of the mixtures.

5. The dielectric constants of all the mixtures fell between those of the ingredients, though far from showing them to be additive quantities. Most of the conductivities did not fall between those of the ingredients.

6. The solutes in almost all cases lowered the dielectric constants more than one would expect on the basis of an additive property.

7. The most marked influence in lowering the dielectric constant was shown by the triethylamine, while ethylcyan acetate showed the greatest tendency to keep the dielectric constant high.


Pyridine and Water
No. 1.
D.C.
Percent pyridine by weight
80
70
60
50
40
30
20
10
0
20
40
60
80
100


Solvent 50% P, 50% W.
No 2.
D.C.
Ethyl Acetate
Aniline
Percent Weight
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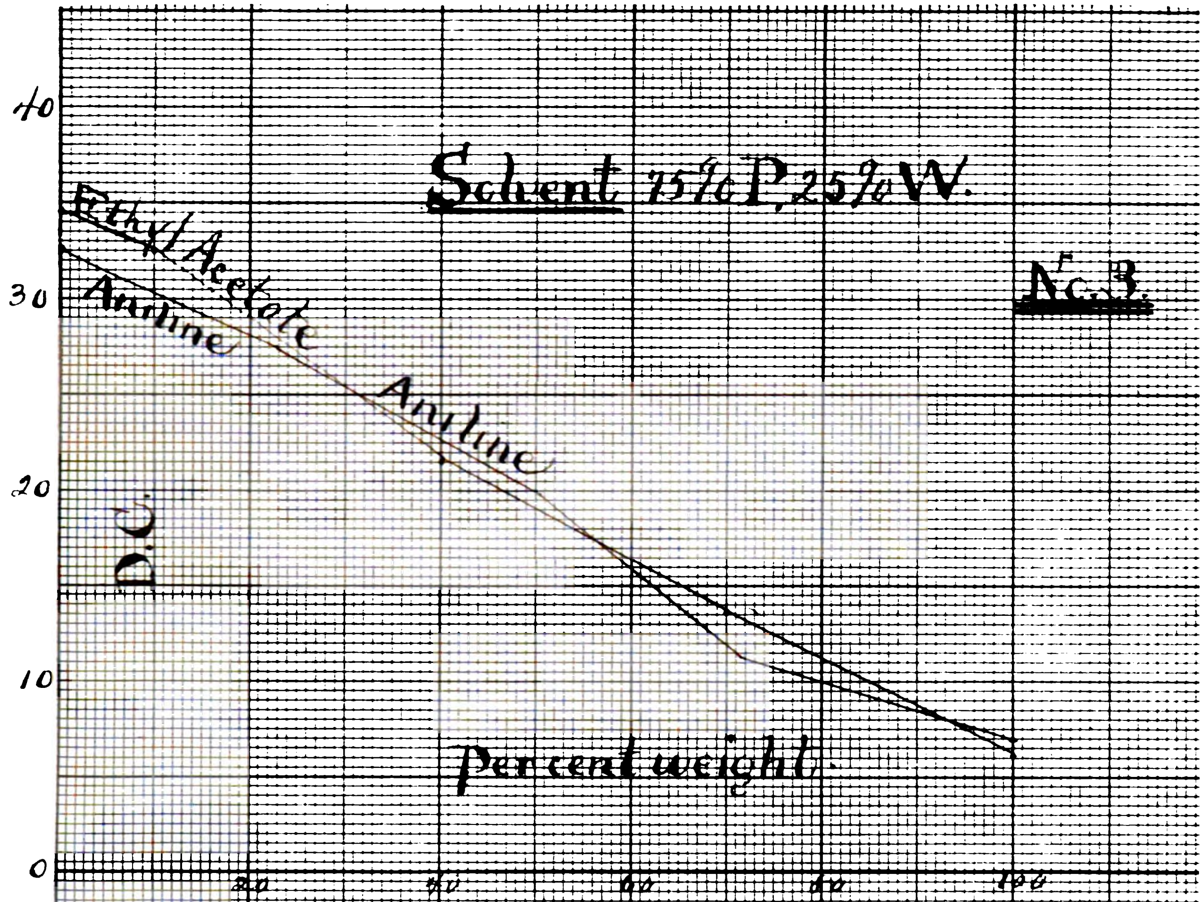
30
20
10
0
20
40
60
80
100


Solvent 75% P, 25% W.
No. 3.
Ethyl Acetate
Aniline
Aniline
D.C.
Percent weight
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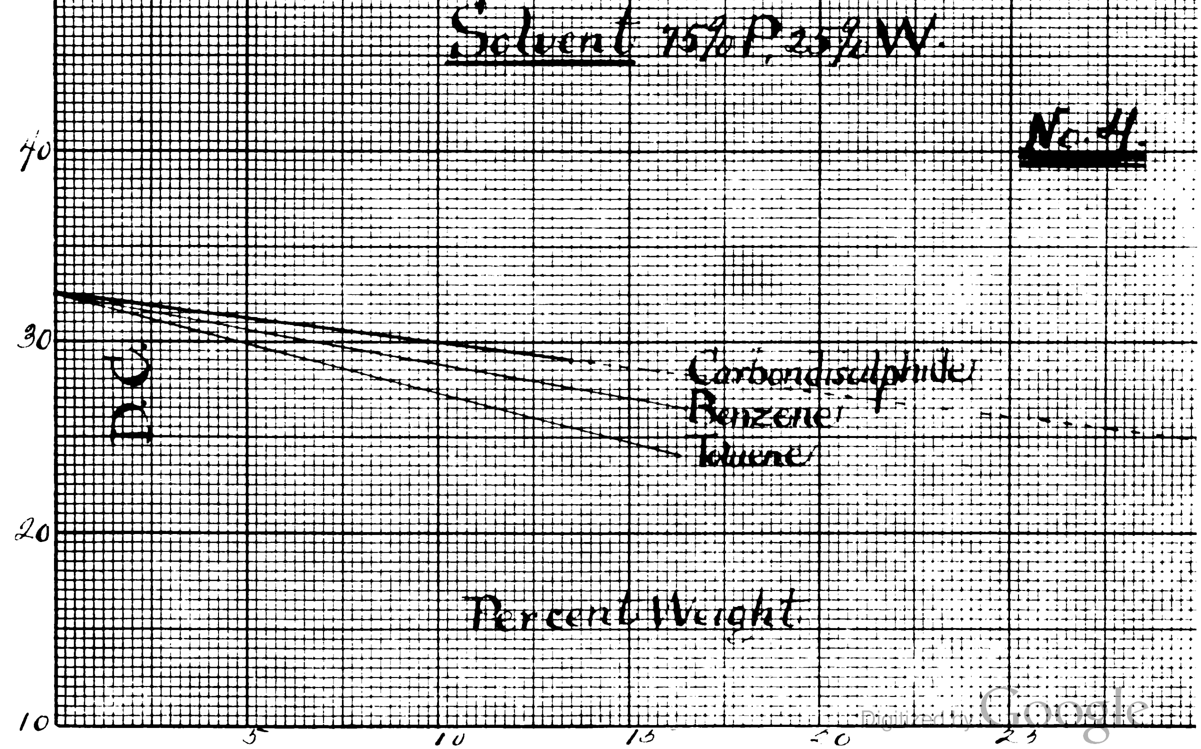
30
20
10
0
20
40
60
80
100


Solvent 75% P, 25% W.
No. 4.
Carbondisulphide
Benzene
Toluene
D.C.
Percent Weight
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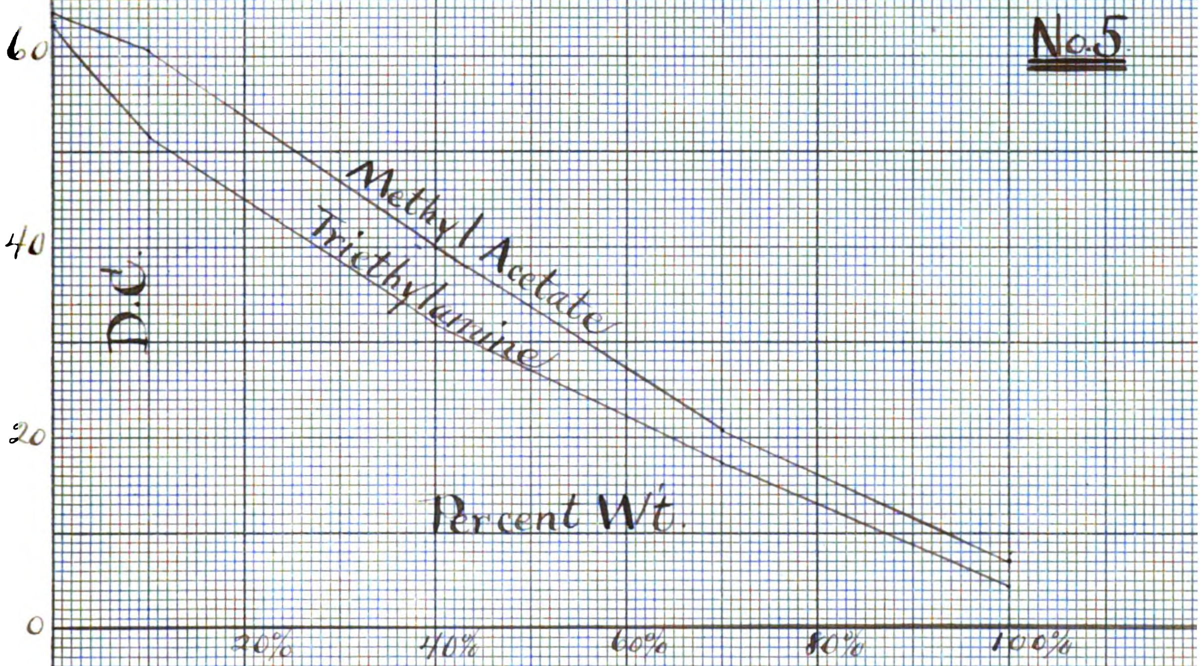
30
20
10
5
10
15
20
25

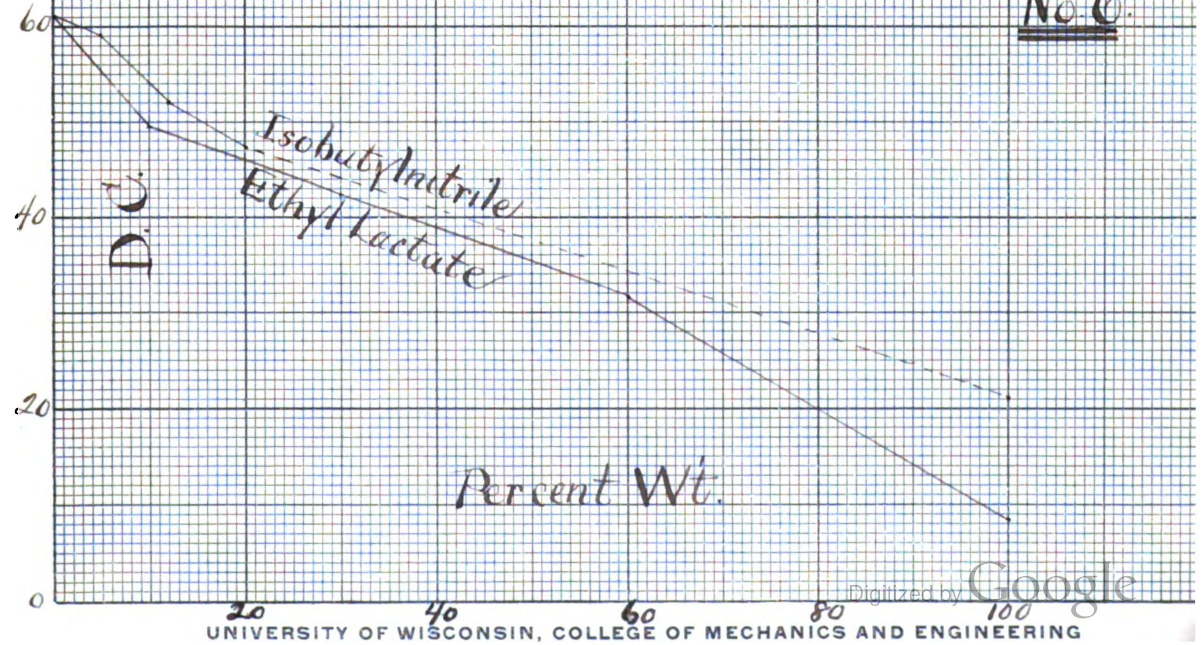
Solvent 25% P, 75% W.

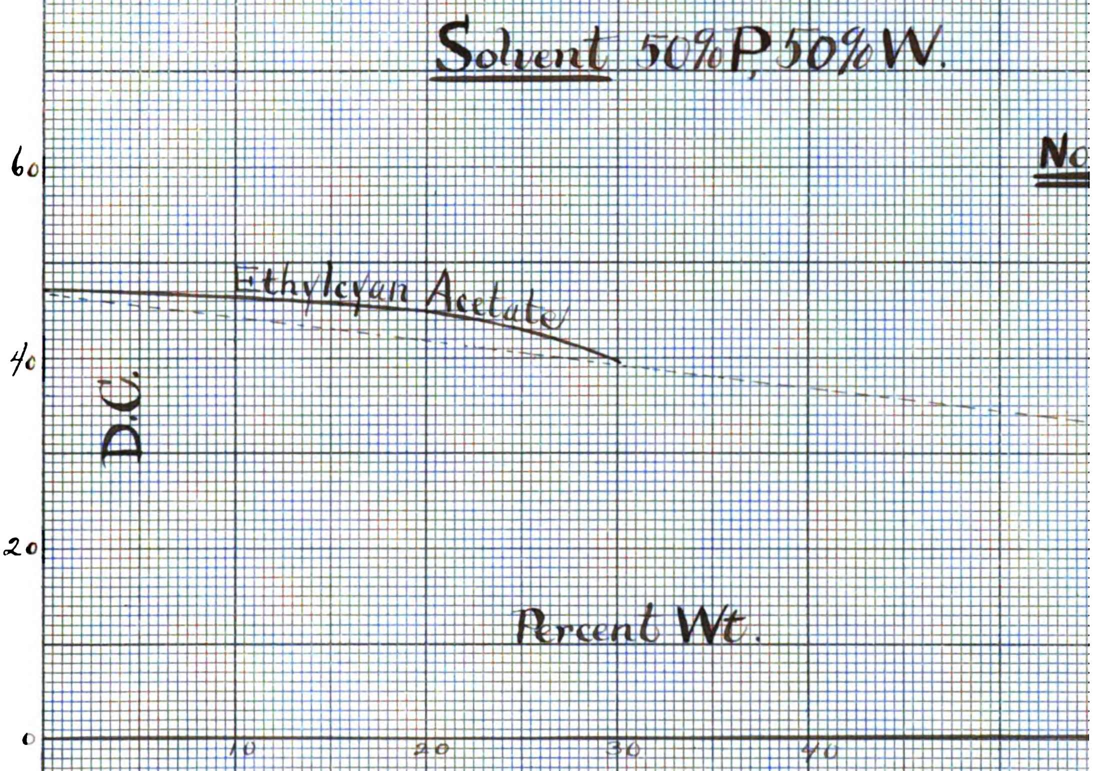
No.5.

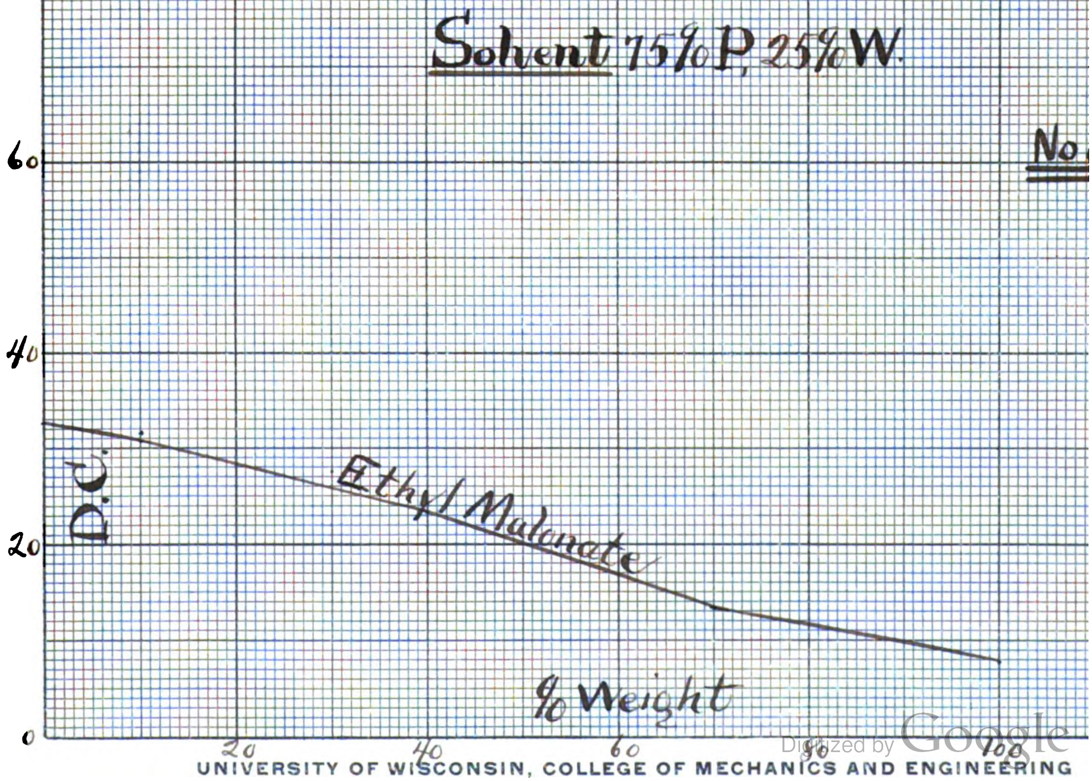


Solvent 75% P, 25% W.

No.6.







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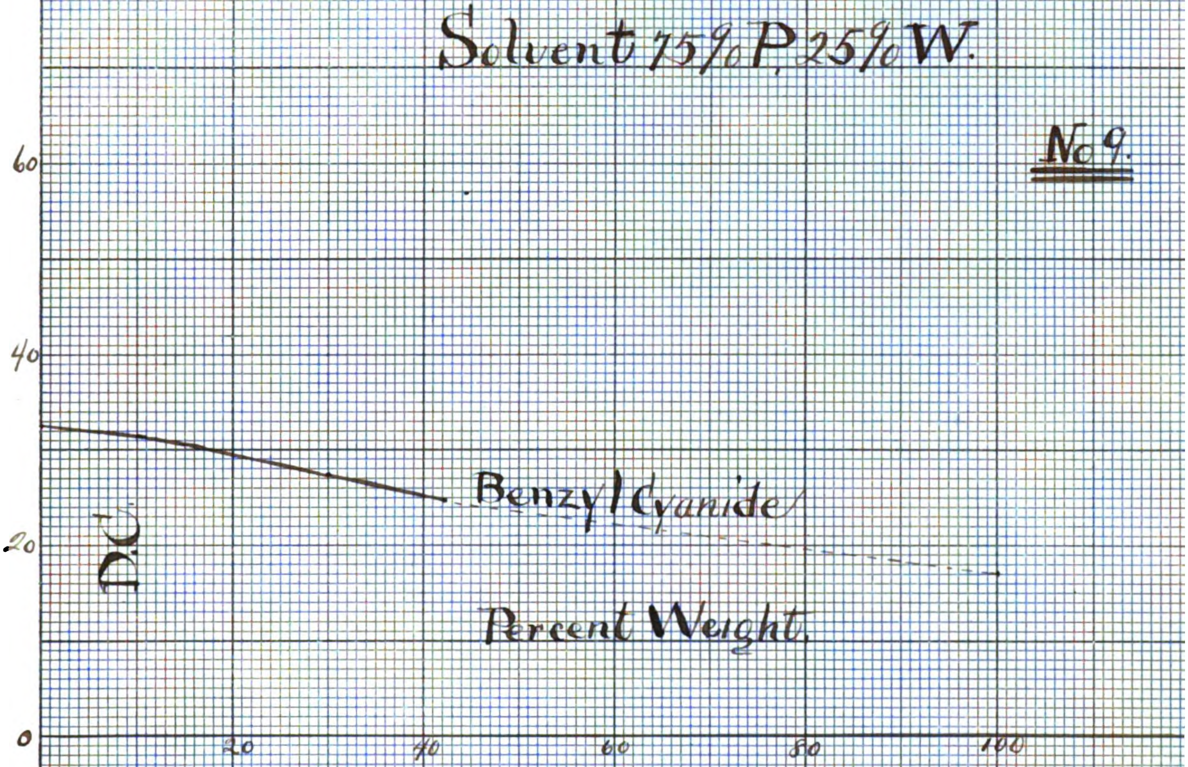
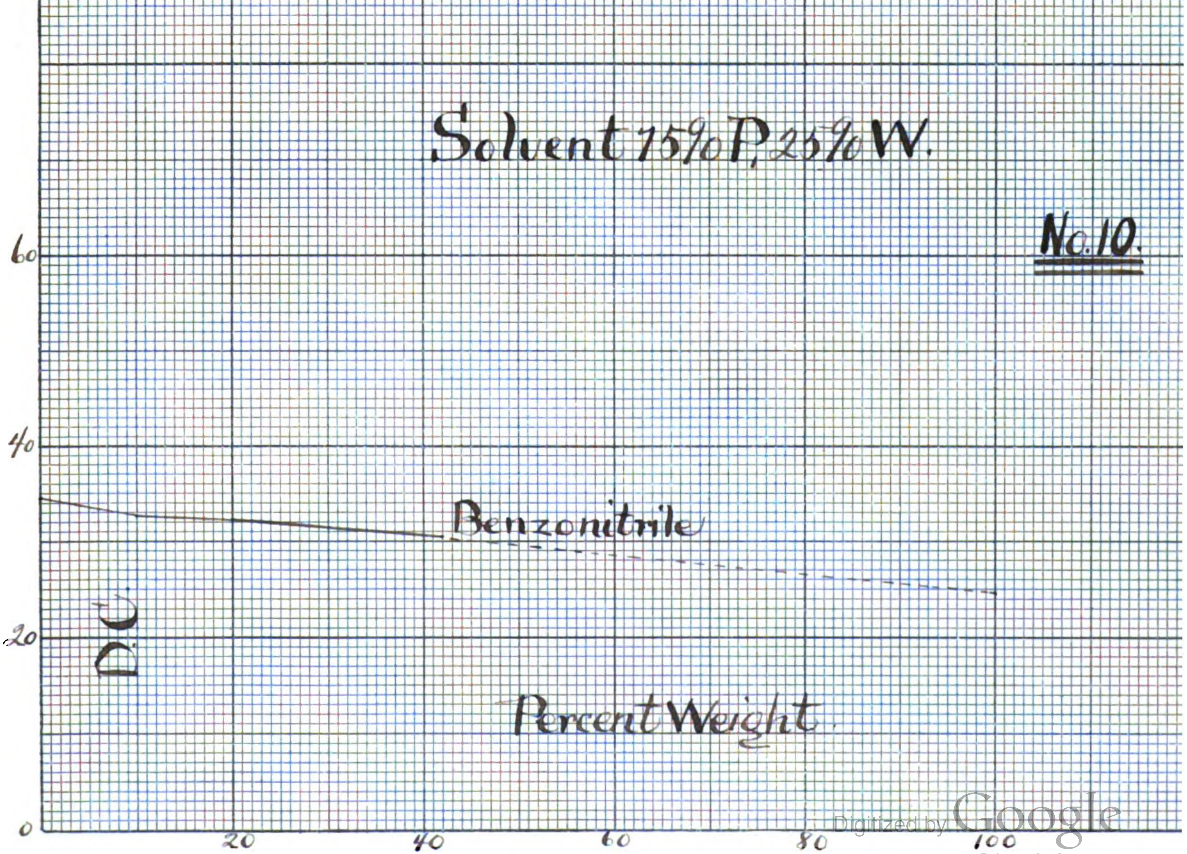


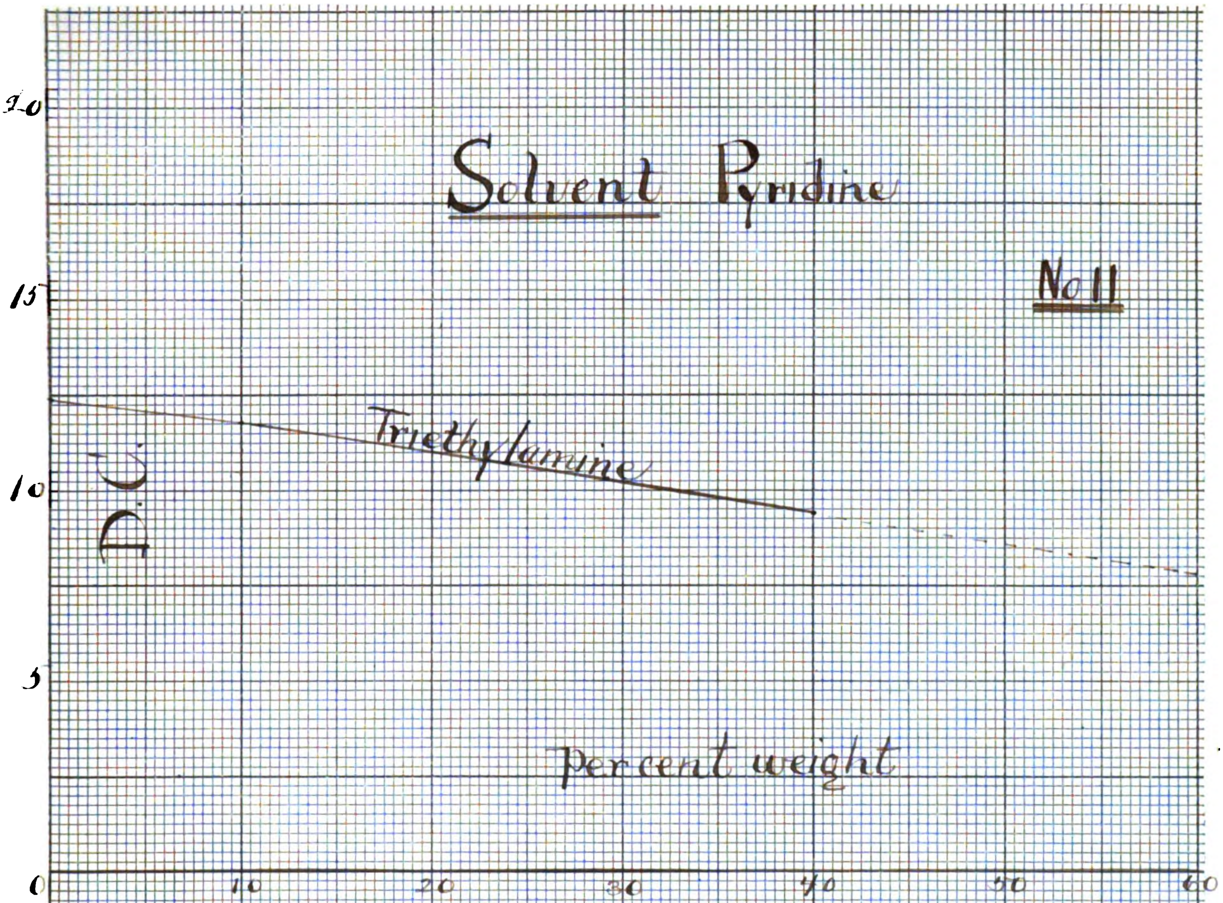
Solvent 75% P, 25% W.

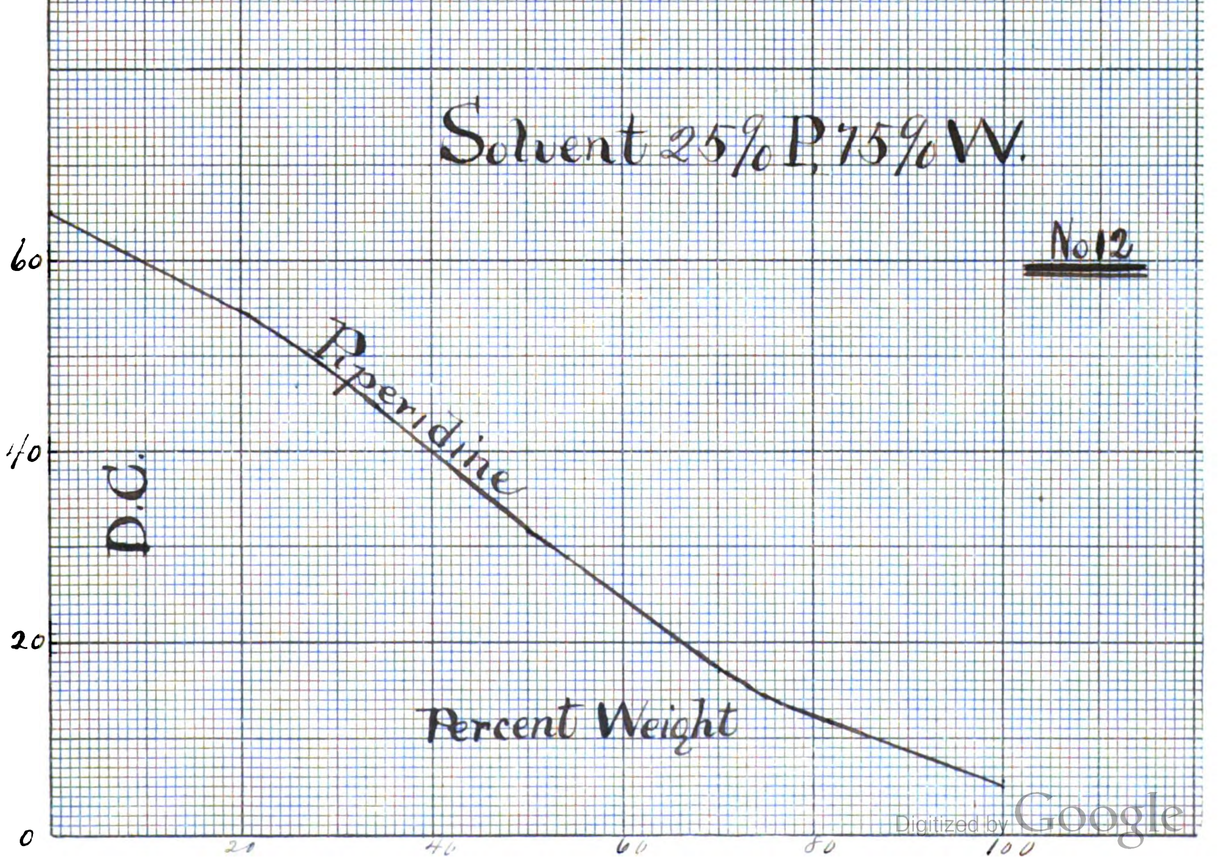
No 9.



Solvent 75% P, 25% W.

No. 10.


Solvent Pyridine
No 11
D.C.
Triethylamine
Percent weight
20
15
10
5
0
10
20
30
40
50
60


Solvent 25% P, 75% W.
No 12
D.C.
Piperidine
Percent Weight
60
40
20
0
20
40
60
80
100

Accepted, June 4, 1907.

L. Kahlenberg.

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